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AUTHOR(S):

Saito, Makina; Kitao, Shinji; Kobayashi, Yasuhiro;
Kurokuzu, Masayuki; Yoda, Yoshitaka; Seto, Makoto

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Slow Processes in Supercooled *o*-Terphenyl: Relaxation and Decoupling

Makina Saito,^{1,2} Shinji Kitao,^{1,2} Yasuhiro Kobayashi,^{1,2} Masayuki Kurokuzu,^{1,2} Yoshitaka Yoda,^{2,3} and Makoto Seto^{1,2}

¹Research Reactor Institute, Kyoto University, Kumatori, Osaka 590-0494, Japan

²CREST, Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan

³Japan Synchrotron Radiation Research Institute, Sayo, Hyogo 679-5198, Japan

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We mapped the relaxation times of inter- and intramolecular correlations in *o*-terphenyl by a quasielastic scattering method using nuclear resonant scattering of synchrotron radiation. From the obtained map, we found that the slow β process is decoupled from the α process at 278 K, and this temperature is clearly below the previous decoupling temperature of 290 K, at which the α -relaxation dynamics changes. Then, it was also concluded that sufficient solidlike condition achieved by further cooling from 290 K is required to decouple the slow β process from the α process and, due to the difference of the length scales between the α and the slow β processes, these two averaged relaxation times $\langle\tau\rangle$ are concluded not to cross as an extrapolation assumed so far. Furthermore, evidence of the restricted dynamics of the slow β process could be obtained as an anomalous momentum transfer (q) dependence of $\langle\tau\rangle(\langle\tau\rangle \propto q^{-2.9})$ at 265 K, observed at q values of 18–48 nm⁻¹.

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The molecular dynamics in glass-forming liquids and polymers toward glass transition has been studied extensively for understanding the nature of the glass transition [1,2]. In particular, the relaxation process known as the α process, which is the structural relaxation process induced by the molecular diffusion, has been thought to be directly related to the glass transition. On the other hand, the nature of the slow β (Johari-Goldstein) process, which seems to be branched from the α process with cooling, has not been fully understood. The slow β process is known to be the universal and essential process in the glass transition phenomenon because the slow β process correlates with the α process and does not always require the internal degree of freedom in molecules, and the branching phenomenon is observed in many glass formers. Moreover, decoupling has been considered to occur at around the temperature at which the change in the α -relaxation dynamics occurs [3]. Therefore, understanding the microscopic mechanisms of the slow β process and its decoupling from the α process is thought to be important in revealing the glass transition mechanism and the microscopic dynamical picture in supercooled liquids. However, the decoupling phenomenon has also not been fully understood yet; for example, how the dielectric spectra should be analyzed around the decoupling region and what causes the different types of the relaxation maps showing the branch of the α - and the slow β -relaxation times [4]. What causes these problems from being solved is partly due to the difficulty of obtaining microscopic information on the decoupling phenomenon using conventional methods such as the dielectric relaxation method, which offers little information on the length scale of the relaxation. On the other hand, the decoupling of the slow β process from the α process in polybutadiene, for example, has been studied using a

neutron spin echo (NSE) method, and the length scales of the relaxation processes have been assigned by selecting a momentum transfer q [5,6]; the obtained results were compared with that obtained from simulations [7]. In these studies, the slow β process was discussed using the hopping model, and its average jump distance was estimated. Moreover, the degree of heterogeneous dynamical behavior was discussed by considering the q dependence of the relaxation time of the α process and the stretching parameter β_{KWW} of the Kohlrausch-Williams-Watts (KWW) function [8]. Therefore, the NSE method is effective for the study of microscopic dynamics. However, owing to limitations on the accessible q and time ranges, the decoupling behavior of the slow β process from the α process and the detailed q dependence of the relaxation time at low temperatures have not been fully examined.

Rayleigh scattering of Mössbauer radiation (RSMR) using a radioactive isotope (RI) has also been used to study microscopic slow dynamics [9]. In this method, a gamma ray is used as a probe for quasielastic scattering measurement in a large q region (on the order of 10 nm⁻¹). However, detailed studies require a long measuring time because of the lack of the directivity of the gamma rays from the RI source. A time-domain interferometry (TDI) method using synchrotron radiation pulses is a time-domain analog of the RSMR method [10–13]. Because it uses a directional beam, the TDI method enables efficient measurement. In this method, two nuclear absorbers placed upstream and downstream of a sample with slightly different nuclear excitation energies each other are used to generate probe and reference gamma rays. Then, the interference beating pattern of these gamma rays is detected in the time domain. The relaxations of the density correlation are reflected as a disappearance of the beating pattern,

which gives the intermediate scattering function $F(q, t)$ [11]. Using TDI, we studied the microscopic dynamic behavior of a typical glass-forming molecule *o*-terphenyl, which has been studied intensively because its nearly spherical molecular shape is favorable for a model system of fragile glass formers [14]. To date, quasielastic scattering experiments on *o*-terphenyl have been performed above 290 K [15–17], which is known to be the crossover temperature of the dynamics and the decoupling temperature of the α and slow β processes [3,17,18]. However, the microscopic dynamical behavior around this temperature is still unclear. This Letter reports new experimental results on the slow microscopic dynamical behavior of *o*-terphenyl and concludes that (i) the obtained decoupling temperature (278 K) is clearly lower than the extrapolated temperature (290 K) assumed to be the decoupling temperature so far and, since the obtained decoupling temperature is also lower than the changing temperature of the diffusion behavior (290 K), our result indicates that sufficient solidlike condition achieved by further cooling from 290 K is required to decouple the slow β process from the α process, (ii) due to the difference of the length scales between the α process and the slow β process, these two averaged relaxation times do not cross as an extrapolation assumed so far, and (iii) evidence of the restricted dynamical behavior of the slow β process could be obtained as an anomalous q dependence of the relaxation time.

The experiments were performed at the nuclear resonant scattering beam line (BL09XU) of SPring-8 in Japan. We have used gamma rays from the first excited state of ^{57}Fe nuclei as a probe and reference beams for a quasielastic scattering measurement; the experimental method and condition of TDI, including nuclear forward scattering, which is used for calibration, are described in detail in the literature [10–13]. TDI time spectra [examples are shown in Fig. 1(a)] were obtained for *o*-terphenyl at temperatures $T = 240, 250, 260, 265, 270, 275, 276, 278.4, 280, 285, 290$, and 300 K at q values of 14 and 23 nm^{-1} , which are the first peak and valley of the static structure factor $S(q)$, respectively, as shown in the inset in Fig. 1(b). The *o*-terphenyl used in the experiments was produced by Tokyo Chemical Industry Co., Ltd.; its glass transition temperature, measured by differential scanning calorimetry (DSC), was 244 K.

The q dependence of the time spectra was observed at 265 K at q values of 14, 18, 23, 29, 35, 41, and 48 nm^{-1} . As shown in Fig. 1, the beating pattern in the time spectra becomes less clear with increasing T or q because the relaxations occur more rapidly as T or q increases. We performed least square fittings using the expressions shown in literature [10–13]. As an intermediate scattering function, the KWW function $F(q, t) \propto \exp\{-(t/\tau)^{\beta_{\text{KWW}}}\}$ was used, with β_{KWW} fixed at 0.6 (the validity of this was confirmed as described later), and the relaxation times τ were obtained. The τ values obtained by fitting were

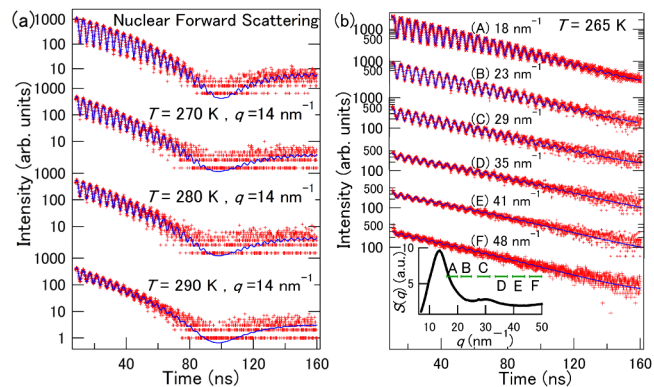


FIG. 1 (color online). Examples of TDI time spectra (+ symbols) and their fitting curves (solid lines) (a) at several T at $q = 14 \text{ nm}^{-1}$ and the nuclear forward scattering spectrum and (b) at several q at 265 K. Inset of (b) shows $S(q)$ (solid line) and the q ranges (bars), which were used for the measurements. The finite size of the q ranges originate from finite solid angles of the detectors. In the measurements, nuclear absorbers of different thicknesses, whose effective thicknesses are about 21 and 10 for the spectra in Figs. 1(a) and 1(b), respectively, were used to optimize the measurement efficiency for the expected relaxation times, and the difference is reflected in the envelope of the time spectra shown in Figs. 1(a) and 1(b).

transformed to the mean relaxation times $\langle\tau\rangle$ using the relation $\langle\tau\rangle = \tau\Gamma(1/\beta_{\text{KWW}})/\beta_{\text{KWW}}$.

When $q = 14 \text{ nm}^{-1}$, the T dependence of $\langle\tau\rangle$ obeys the Vogel-Fulcher-Tammann (VFT) law $\langle\tau(T)\rangle \propto \exp\{DT_0/(T - T_0)\}$, as shown in Fig. 2, where T_0 is the Vogel-Fulcher temperature, and D is the fragility index. The parameters [$D = 3.1(3)$, $T_0 = 235(26) \text{ K}$] obtained by the least squares fitting and the time scale of $\langle\tau\rangle$ are

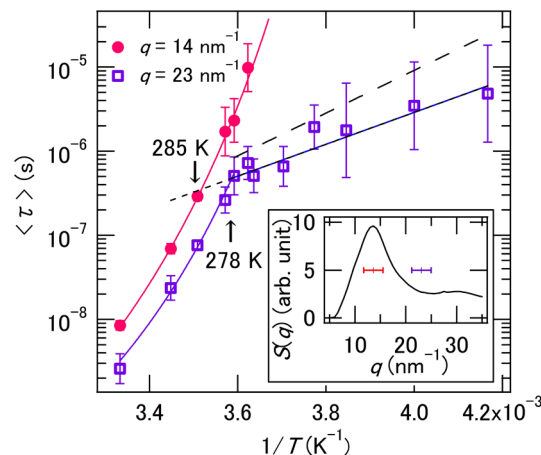


FIG. 2 (color online). T dependence of $\langle\tau\rangle$ at $q = 14$ and 23 nm^{-1} . Solid lines show the fitting curves as discussed in the main text. Short and long dashed lines show the extrapolation of the Arrhenius fitting curve and the dielectric relaxation time of the slow β process [22], respectively. The $S(q)$ (solid line) and q regions (bars) used for the measurements are shown in the inset.

consistent with those reported for the α process [3,19,20]. This result indicates that the relaxation observed at $q = 14 \text{ nm}^{-1}$ is due to the α process and is the one with the mean α -relaxation time. Because the corresponding first peak position of $S(q)$ reflects the intermolecular correlation, it is confirmed that this structural relaxation is the α process. On the other hand, at $q = 23 \text{ nm}^{-1}$ reflecting correlations with the length scale less than the intermolecular distance, the character of the T dependence of $\langle\tau\rangle$ was found to change at 278 K, as shown in Fig. 2. Such a change has been observed in polybutadiene [5]. The T dependence of $\langle\tau\rangle$ obeys the VFT law above 278 K but obeys the Arrhenius law $\langle\tau(T)\rangle \propto \exp\{E/T\}$ below 278 K where E denotes the activation energy. The E value of 36(9) kJ/mol obtained by least square fitting is consistent with those of the slow β process obtained by the dielectric method [18,21,22]. Therefore, the relaxations observed at $q = 23 \text{ nm}^{-1}$ below 278 K are mainly due to the slow β process and the slow β process occurs at the local length scale in *o*-terphenyl. Because the behavior of the T dependence of $\langle\tau\rangle$ above 278 K at $q = 23 \text{ nm}^{-1}$ is similar to that at $q = 14 \text{ nm}^{-1}$, the relaxation observed at $q = 23 \text{ nm}^{-1}$ above 278 K is mainly due to the α process. Therefore, the turning temperature of 278 K is interpreted to be the decoupling temperature $T_{\alpha\beta}$ at which the primary source of the relaxation process observed at $q = 23 \text{ nm}^{-1}$ changes from the α process to the slow β process with cooling. The value of β_{KWW} has already been determined to be 0.6 for q values ranging from 5 to 40 nm^{-1} at $T > 290 \text{ K}$ [15]. From our experiment, the values of β_{KWW} for the obtained relaxation function were determined to be 0.64 (15) for 14 nm^{-1} at 285 K and 0.56 (31) at 265 K for q values ranging from 27 to 50 nm^{-1} . Therefore, within the experimental errors, the previously obtained β_{KWW} value of 0.6 was confirmed to be consistent with the values at both 285 and 265 K, at which the primary source of the relaxation was considered to be the α and the slow β processes, respectively. Therefore, we adopted a β_{KWW} value of 0.6, which is the more precise value obtained above 290 K [15] for all measured T and q ranges in order to obtain the relaxation time consistently.

At q above the first peak of $S(q)$, a simulation study showed that the relaxation of the density correlation is caused by relaxations of not only intramolecular but also intermolecular correlations [23]. Experimentally, we examined whether the α and the β processes coexist at $T \leq T_{\alpha\beta}$ and at q above the peak of $S(q)$; we tried to use the relaxation function $F(t) = F_{\alpha}(t)F_{\beta}(t)$, which is a product of the relaxation functions of the α and the slow β processes, to analyze the time spectrum obtained at 278.4 K and $q = 23 \text{ nm}^{-1}$ [6,24], because, at around the decoupling temperature (278 K), both processes are expected to be seen. However, as a result of the fitting, the two relaxation processes could not be resolved even if they coexisted within the experimental accuracy. Therefore, we

could not determine whether the correlation at length scales shorter than the intermolecular scale relaxes by not only the slow β process but also the α process at $T \leq T_{\alpha\beta}$. However, the $\langle\tau\rangle$ value obtained at a much lower T than $T_{\alpha\beta} \sim 278 \text{ K}$ at $q = 23 \text{ nm}^{-1}$ originates mainly in the slow β process. This is because the relaxation time of the α process, even if it exists, is expected to be much longer than that of the slow β process considering the temperature dependence of the α -relaxation time at high temperatures; therefore, it can be neglected in our measuring range. Moreover, the obtained E value is consistent with those obtained previously [18,21,22], as discussed above. The obtained decoupling temperature of 278 K is believed to be not greatly affected by the uncertainty of the model of $F(t)$ because the extrapolation of the slow β -relaxation time from the lower temperature side, which is reliable, also indicates a decoupling temperature of approximately 278 K. Therefore, the obtained decoupling temperature of 278 K is lower than the 290 K value that has been considered to be the decoupling temperature thus far.

Moreover, as shown in Fig. 2, we are aware that the crossover point of the extrapolation of the Arrhenius law obtained at 23 nm^{-1} and the VFT law obtained at 14 nm^{-1} is approximately 285 K, which is close to the previous decoupling temperature of 290 K. The decoupling temperature of the α and the slow β processes has typically been determined by extrapolating the relaxation times of the slow β process to the mean relaxation times of the α process. However, our experimental study clearly revealed that the slow β -relaxation process splits from the relaxation process of the local length scale originating in the α process, which is shorter than the mean relaxation time of the α process and due to the difference of the length scales between the α and the slow β processes, these two averaged relaxation times are concluded not to cross as an extrapolation assumed so far. Furthermore, since the obtained decoupling temperature is also lower than the changing temperature of the diffusion behavior (290 K), our result indicates that sufficient solidlike condition achieved by further cooling from 290 K is required to decouple the slow β process from the α process [25].

Because the q dependence of the slow β -relaxation time at relatively low T and high q is expected to reveal the properties of the slow β process, we measured the q dependence of $\langle\tau\rangle$ at 265 K (below $T_{\alpha\beta}$) and at q values above the peak of $S(q)$, at which the spatial correlation relaxes mainly by the slow β process. In both the self- and mutual correlation functions, the q dependence of $\langle\tau\rangle$ in liquids is known to follow $\langle\tau\rangle \propto q^{-2}$, indicating that molecules diffuse relatively freely. This relation has been confirmed for *o*-terphenyl at T above 290 K [15,16,26]. However, toward the glass transition, the dynamical behavior of the molecules is expected to change from liquidlike to glasslike. In fact, our result shown in Fig. 3 indicates that the $\langle\tau\rangle$ value obtained at 48 nm^{-1} is approximately 2 times

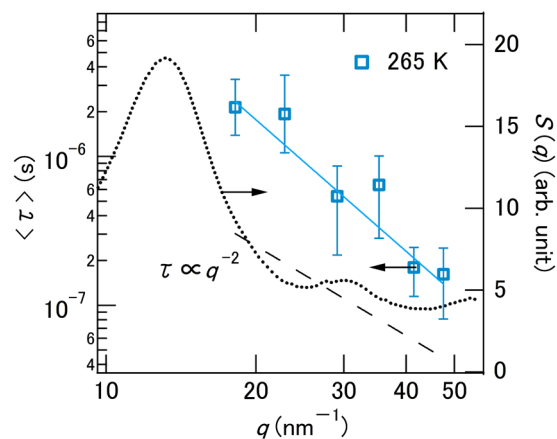


FIG. 3 (color online). q dependence of $\langle \tau \rangle$ at $T = 265$ K (square symbols) and the static structure factor (dot line). The solid line shows its fitting curve. The dashed line shows the q^{-2} behavior of $\langle \tau \rangle$.

shorter than the value predicted by the relation $\langle \tau \rangle \propto q^{-2}$ and the $\langle \tau \rangle$ value obtained at 18 nm^{-1} . To detect the anomalous dynamical behavior at $T = 265$ K below $T_{\alpha\beta}$, the q dependence of $\langle \tau \rangle$ was investigated by fitting with the power law $\langle \tau \rangle \propto q^{-n}$, where n is the power law index. Fittings were performed at $q = 18\text{--}48 \text{ nm}^{-1}$ where the effect of de Gennes narrowing can be neglected [16], as shown in Fig. 3, and we could obtain an n value of 2.9 (5). Using the power law index, the time dependence of the mean squared displacements is expressed as $\langle \Delta r^2(t) \rangle \propto t^{2/n}$ for translational diffusion [8], where $\Delta r(t)$ is the displacement of a molecular position within t . For temperatures at which $n > 2$, the mean squared displacement becomes sublinear in time, indicating restricted molecular motions. Therefore, the obtained n value greater than 2 indicates the restricted microscopic dynamical behavior of the slow β process, which is independent of the origin. The sublinear mean squared displacement in time is similar to the result obtained in a concentrated colloidal system [27]. Then, this restricted dynamical picture of the slow β process is consistent with the results obtained from NMR measurements [28]. Therefore, the evidence of the restricted dynamics of the slow β process could be obtained as an anomalous q dependence of $\langle \tau \rangle$ by the quasielastic scattering method. Then, our approach enables us to study how the restricted motion starts to occur around the decoupling temperature in the future and to study the relationship between the decoupling temperature and the changing temperature of the diffusion dynamics more clearly. As the origin of the slow β process in *o*-terphenyl, the rotation of the phenyl ring has been proposed [29]. Moreover, a small rearrangement of the entire molecule, which was attributed to the slow β process in a similar small-molecule liquid, may also contribute to the slow β process in *o*-terphenyl [30]. Since both motions can cause relaxation of the intramolecular correlation, both of the interpretations are consistent with our experimental

result. Colmenero *et al.* proposed that the degree of dynamical heterogeneity x can be estimated by the relation $n = 2x/\beta_{\text{KWW}}$ [8]. For *o*-terphenyl at 265 K, x could be estimated to be 0.87. Therefore, under their interpretation, dynamical heterogeneity causes less than half of the stretching degree of the relaxation function. Finally, we consider why the $\langle \tau \rangle$ value obtained at the first peak of $S(q)$ follows the VFT law and does not seem to be obviously affected by the slow β process. For *o*-terphenyl, the correlation of phenyl rings belonging to different molecules contributes to the first peak of $S(q)$ [23]. Therefore, at high temperatures, the intermolecular correlation is thought to also be affected by the rotation of the phenyl rings. However, at a low temperature such as 265 K, the relaxation of the intermolecular correlation is not induced by the rotation as much because the intramolecular motions occur in a restricted length scale as shown above, and do not contribute as much to the relaxation of the intermolecular correlation.

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